

HYDROGEN STORAGE SYSTEM MATERIALS AND METHODS INCLUDING HYDRIDES AND HYDROXIDES

FIELD OF THE INVENTION

[0001] The present invention relates to hydrogen storage compositions, the method of making such hydrogen storage compositions and use thereof.

BACKGROUND OF THE INVENTION

[0002] Hydrogen is desirable as a source of energy because it reacts cleanly with air producing water as a by-product. In order to enhance the desirability of hydrogen as a fuel source, particularly for mobile applications, it is desirable to increase the available energy content per unit volume and per unit mass of storage. Presently, this is done by conventional means such as storage under high pressure, at thousands of pounds per square inch (e.g., 5,000 to 10,000 psi), cooling to a liquid state, or absorbing into a solid such as a metal hydride. Pressurization and liquification require relatively expensive processing and storage equipment.

[0003] Storing hydrogen in a solid material such as metal hydrides, provides volumetric hydrogen density which is relatively high and compact as a storage medium. Binding the hydrogen as a solid is desirable since it desorbs when heat is applied, thereby providing a controllable source of hydrogen .

[0004] Rechargeable hydrogen storage devices have been proposed to facilitate the use of hydrogen. Such devices may be relatively simple and

generally are simply constructed as a shell and tube heat exchanger where the heat transfer medium delivers heat for desorption. Such heat transfer medium is supplied in channels separate from the chamber which houses the hydrogen storage material. Therefore, when hydrogen release is desired, fluids at different temperatures may be circulated through the channels, in heat transfer relationship with the storage material, to facilitate release of the hydrogen. For certain materials, recharging the storage medium can be achieved by pumping hydrogen into the chamber and through the storage material while the heat transfer medium removes heat, thus facilitating the charging or hydrogenating process. An exemplary hydrogen storage material and storage device arranged to provide suitable heat transfer surface and heat transfer medium for temperature management is exemplified in U.S. Patent No. 6,015,041.

[0005] Presently, the selection of relatively light weight hydrogen storage material is essentially limited to magnesium and magnesium-based alloys which provide hydrogen storage capacity of several weight percent, essentially the best known conventional storage material with some reversible performance. However, such magnesium based materials have a limitation in that they take up hydrogen at very high temperature and high hydrogen pressure. In addition, hydrogenation of the storage material is typically impeded by surface oxidation of the magnesium. Other examples, such as LaNi₅ and TiFe, have relatively low gravimetric hydrogen storage density, since they are very heavy.

[0006] Therefore, in response to the desire for an improved hydrogen storage medium, the present invention provides an improved hydrogen storage composition, its use as a storage medium and a method for forming such materials.

SUMMARY OF THE INVENTION

[0007] In one aspect, the invention provides a method of producing hydrogen comprising reacting a first portion of a hydride with water to produce heat and causing a second reaction between a second portion of the hydride and a hydroxide, by transferring the heat thereto.

[0008] In another aspect, the invention provides a method of producing hydrogen comprising: generating heat in a first reaction by reacting water with a portion of a hydride present in a first material composition, wherein the heat is used in a hydrogen production reaction. A remaining portion of the hydride present in the first material composition is reacted with a hydroxide present in a second material composition in the hydrogen production reaction, thereby forming a hydrogen product and a byproduct composition comprising an oxide.

[0009] In still another aspect of the invention, there is provided a hydrogen storage composition having a hydrogenated state and a dehydrogenated state: where in the hydrogenated state, the composition comprises a hydride and a hydrated hydroxide; and in the dehydrogenated state, the composition comprises an oxide.

[0010] Further areas of applicability of the present invention will become apparent from the detailed description provided hereinafter. It should be understood that the detailed description and specific examples, while indicating the preferred embodiment of the invention, are intended for purposes of illustration only and are not intended to limit the scope of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The present invention will become more fully understood from the detailed description and the accompanying drawings, wherein:

[0012] Figure 1 shows hydrogen production by weight percent loss of hydrogen from a hydrogen storage material comprising lithium hydride and lithium hydroxide analyzed by a modified volumetric Sievert's apparatus analysis;

[0013] Figure 2 is a graph showing hydrogen production for a hydrogen storage material comparing a first sample comprising lithium hydride and lithium hydroxide and a second sample comprising lithium hydride, lithium hydroxide, and a catalyst, where temperature is incrementally increased in a modified Sievert's apparatus;

[0014] Figure 3 is a graph showing hydrogen production over time for a hydrogen storage material comprising sodium hydride and lithium hydroxide from a modified Sievert's apparatus analysis; and

[0015] Figure 4 is a graph showing hydrogen production over time for a hydrogen storage material comprising a complex hydride of lithium borohydride and lithium hydroxide from a modified Sievert's apparatus analysis.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] The following description of the preferred embodiment(s) is merely exemplary in nature and is in no way intended to limit the invention, its application, or uses.

[0017] In one aspect, the present invention provides a system for producing and releasing hydrogen from a hydrogen storage material system. In one preferred embodiment, a method is provided for releasing hydrogen from hydrogen storage materials by conducting a first reaction between a first portion of a hydride composition and water. This first reaction generates heat, which is used to initiate a second hydrogen production reaction. The hydrogen production reaction is conducted by reacting a hydride composition and a hydroxide composition. The hydrogen production reaction produces hydrogen and a reaction byproduct comprising an oxide composition. As used herein, the term "composition" refers broadly to a substance containing at least the preferred chemical compound, but which may also comprise additional substances or compounds, including impurities. The term "material" also broadly refers to matter containing the preferred compound or composition. Other preferred embodiments of the present invention relate to methods of releasing hydrogen from hydrogen storage compositions, as will be discussed in greater detail below.

[0018] In another aspect, the present invention provides hydrogen storage materials. In one preferred embodiment of the present invention, a hydrogen storage composition has a hydrogenated state and a dehydrogenated state, therein providing two distinct physical states where hydrogen can be stored and subsequently released. In the hydrogenated state, the composition comprises a hydride and a hydroxide. In the dehydrogenated state, the composition comprises an oxide. The hydrated hydroxide compound reacts with

a portion of the hydride to generate heat sufficient to initiate a dehydrogenation reaction resulting in the dehydrogenated product.

[0019] In one preferred embodiment of the present invention, the hydride is represented by the general formula MI^xH_x , where MI represents one or more cationic species other than hydrogen, and x represents the average valence state of MI, where the average valence state maintains the charge neutrality of the compound.

[0020] In another preferred embodiment of the present invention, the hydroxide is represented by the general formula $\text{MII}^y(\text{OH})_y$, where MII represents one or more cationic species other than hydrogen, and y represents the average valence state of MII where the average valence state maintains the charge neutrality of the compound.

[0021] In yet another preferred embodiment of the present invention, the hydride composition is represented by MI^xH_x and the hydroxide composition is represented by $\text{MII}^y(\text{OH})_y$, where MI and MII respectively represent one or more cationic species other than hydrogen, and x and y represent average valence states of MI and MII, and where the average valence states maintain the charge neutrality of the compounds, respectively.

[0022] In accordance with the present invention, MI and MII each represent one or more of a cationic species or a mixture of cationic species other than hydrogen. It should be noted that MI and MII are independently selected from one another. Thus, the present invention contemplates MI and MII comprising the same cationic species, or in alternate preferred

embodiments, MI and MII comprise distinct cationic species that are different from one another. Further, MI, MII, or both may be selected to be complex cations, which comprise two or more distinct cationic species. In the case where MI, MII, or both are complex cations, MI and MII may comprise one or more of the same cationic species, or may have entirely distinct cationic species from one another. Hydrides are often referred to as complex hydrides, which are further contemplated in the present invention. A complex hydride comprises two cationic species, however one of the cationic species forms an anionic group with hydrogen, which further interacts with a second cationic species. This concept can be expressed by the following formula with a hydride expressed as MI^xH_x , where MI comprises two distinct cationic species, M' and M'', so that $MI = M' + M''$. Thus, the hydride can be expressed as: $M_d^{a'}(M''^bH_c)^{-d}$ where (M''^bH_c) is an anionic group, where $d = (c - b)$ and a, b, c, and d are selected so as to maintain charge balance and electroneutrality of the compound. Cationic species that are preferred for all the preferred embodiments of the present invention include metal cations, as well as non-metal cations such as boron. Further, MII is also optionally selected to be an organic cationic group non-metal cation, such as CH_3 .

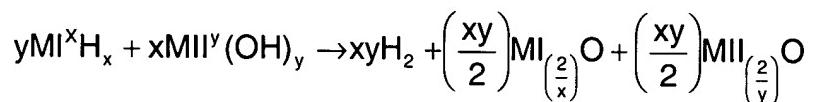
[0023] Elements that form preferred cations and mixtures of cations for MI and MII in the type of compounds of the present invention are as follows. For both hydrides and hydroxides, certain preferred cationic species comprise: aluminum (Al), boron (B), barium (Ba), beryllium (Be), calcium (Ca), cesium (Cs), potassium (K), lithium (Li), magnesium (Mg), sodium (Na), rubidium (Rb),

silicon (Si), strontium (Sr), titanium (Ti), vanadium (V), and mixtures thereof. Particularly preferred elements comprise: aluminum (Al), boron (B), beryllium (Be), calcium (Ca), potassium (K), lithium (Li), magnesium (Mg), sodium (Na), strontium (Sr), titanium (Ti), and mixtures thereof. The most preferred cationic species are Li and Na. Evaluation of the aforesaid known species produces, by analogy, the following added cationic species besides those recited above which are thought to be usable based on predictive thermodynamics, but not yet demonstrated, include arsenic (As), cadmium (Cd), cerium (Ce), europium (Eu), iron (Fe), gallium (Ga), gadolinium (Gd), germanium (Ge), hafnium (Hf), mercury (Hg), indium (In), lanthanum (La), manganese (Mn), neodymium (Nd), nickel (Ni), lead (Pb), praseodymium (Pr), antimony (Sb), scandium (Sc), selenium (Se), samarium (Sm), tin (Sn), thorium (Th), thallium (Tl), tungsten (W), yttrium (Y), ytterbium (Yb), zinc (Zn), zirconium (Zr). For MII, another feasible cationic species comprises low molecular weight organic groups, such as methyl (CH_3), ethyl (C_2H_5), and propyl (C_3H_7) groups.

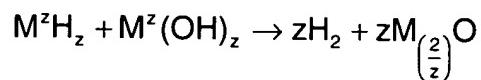
[0024] In view of the above, the cationic species MI or MII generally comprise: aluminum (Al), arsenic (As), boron (B), barium (Ba), beryllium (Be), calcium (Ca), cadmium (Cd), cerium (Ce), cesium (Cs), copper (Cu), europium (Eu), iron (Fe), gallium (Ga), gadolinium (Gd), germanium (Ge), hafnium (Hf), mercury (Hg), indium (In), potassium (K), lanthanum (La), lithium (Li), magnesium (Mg), manganese (Mn), sodium (Na), neodymium (Nd), nickel (Ni), lead (Pb), praseodymium (Pr), rubidium (Rb), antimony (Sb), scandium (Sc), selenium (Se), silicon (Si), samarium (Sm), tin (Sn), strontium (Sr), thorium (Th),

titanium (Ti), thallium (Tl), tungsten (W), yttrium (Y), ytterbium (Yb), zinc (Zn), and zirconium (Zr). Additionally, MII may comprise an organic cationic species, such as methyl (CH_3), ethyl (C_2H_5), and propyl (C_3H_7) groups.

[0025] In preferred embodiments of the present invention, a solid-state hydride composition (i.e., in particulate form) reacts with a hydroxide composition (i.e., in particulate form) via a solid-state reaction to produce and release gaseous hydrogen and a solid-state byproduct compound comprising an oxide. Where the hydride composition is selected as MI^xH_x and the hydroxide composition is selected as $\text{MII}^y(\text{OH})_y$, the hydrogen production reaction proceeds by the following reaction mechanism:



where as previously discussed, x is the average valence state of MI and y is the average valence state of MII where the average valence states maintain the charge neutrality of the respective compounds. Thus, the hydrogenated state of the hydrogen storage composition corresponds to the hydrogenated hydride and hydrogenated hydroxide, and the dehydrogenated hydrogen storage composition corresponds to the one or more byproduct compounds comprising an oxide. It should be noted that where MI and MII are the same cationic species, which can be represented by M, the above reaction mechanism can be simplified to:



where z represents the average valence state of M, where the average valence state maintains the charge neutrality of the compound.

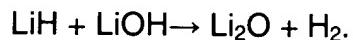
[0026] According to the present invention, it is preferred that at least one byproduct composition comprises an oxide having one or more cationic species of the hydroxide and hydride (i.e., MI, MII, or both). The independent selection of cationic species can vary the stoichiometry of the reaction and the types of byproduct compounds formed. It should be noted that the oxide byproduct compounds $\text{MI}_{\frac{2}{x}}\text{O}$ and $\text{MII}_{\frac{2}{y}}\text{O}$ (or $\text{M}_{\frac{2}{z}}\text{O}$ in the case where MI and MII are the same cation M) may thermodynamically favor forming and/or decomposing into different byproduct compounds. Further, with certain reactants and stoichiometry of the reactants, such oxide byproduct compounds may also comprise higher-order complex hydrides, for example, as will be described in more detail below. These further byproducts are formed of the same general constituents as the primary byproducts, but they have different valence states, atomic ratios, or stoichiometry, depending on the cationic species involved, as recognized by one of skill in the art.

[0027] In certain preferred embodiments of the present invention the hydrogen storage composition comprises a hydride selected from the group consisting of: lithium hydride (LiH), sodium hydride (NaH), potassium hydride (KH), beryllium hydride (BeH₂), magnesium hydride (MgH₂), calcium hydride (CaH₂), strontium hydride (SrH₂), titanium hydride (TiH₂), aluminum hydride (AlH₃), boron hydride (BH₃), and mixtures thereof. Particularly preferred hydride compositions comprise LiH or NaH.

[0028] In alternate preferred embodiments of the present invention the hydrogen storage composition comprises a hydride which is a complex hydride selected from the group consisting of: lithium borohydride (LiBH_4), sodium borohydride (NaBH_4), magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$), calcium borohydride ($\text{Ca}(\text{BH}_4)_2$), lithium alanate (LiAlH_4), sodium alanate (NaAlH_4), magnesium alanate ($\text{Mg}(\text{AlH}_4)_2$), calcium alanate ($\text{Ca}(\text{AlH}_4)_2$), and mixtures thereof. Particularly preferred complex hydrides comprise lithium borohydride (LiBH_4), sodium borohydride (NaBH_4), lithium alanate (LiAlH_4), and sodium alanate (NaAlH_4).

[0029] Further, other preferred embodiments of the present invention, comprise a hydroxide composition selected from the group consisting of: lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), beryllium hydroxide ($\text{Be}(\text{OH})_2$), magnesium hydroxide ($\text{Mg}(\text{OH})_2$), calcium hydroxide ($\text{Ca}(\text{OH})_2$), strontium hydroxide ($\text{Sr}(\text{OH})_2$), titanium hydroxide ($\text{Ti}(\text{OH})_2$), aluminum hydroxide ($\text{Al}(\text{OH})_3$), boron hydroxide ($\text{B}(\text{OH})_3$) which is also known as boric acid and more conventionally is expressed as (H_3BO_3), and mixtures thereof. Particularly preferred hydroxide compounds comprise LiOH and NaOH .

[0030] Thus, according to one preferred embodiment of the present invention, a hydrogen production reaction is conducted by reacting a hydride comprising LiH with a hydroxide comprising LiOH . The reaction proceeds according to the reaction mechanism:



This reaction produces a theoretical 6.25 weight % of hydrogen on a material basis.

[0031] In an alternate preferred embodiment of the present invention a hydrogen production reaction occurs by reacting a hydride comprising NaH with a hydroxide comprising LiOH. The reaction mechanism for this reaction can be expressed as



This reaction generates a theoretical 4.1 weight % hydrogen on a material basis. It should be noted that the byproduct compounds are generally expressed as Li₂O and Na₂O, however, mixed or partially mixed metal oxides may form based on the conditions at which the reaction takes place, and may be thermodynamically favored. Thus, for example, the byproduct composition may comprise an oxide composition comprising a mixed cation oxide ($\text{MI}^x\text{MII}^y\frac{2}{x+y}\text{O}$) formed as a byproduct, where x and y are the average valence states of MI and MII, respectively, and where the average valence state maintains the charge neutrality of the compound. In such a case, the above reaction may form LiNaO as a byproduct compound. The mixed cation oxide byproduct compound may comprise the entire oxide product, or may be mixed with the single cation oxides to result in multiple distinct oxide byproduct compounds, depending on the thermodynamics of the reaction.

[0032] In certain preferred embodiments of the present invention, the reaction mechanism for producing hydrogen from the hydride and hydroxide is reversible. By "reversible" it is meant that a species of a starting material

hydroxide or hydride is regenerated at temperature and pressure conditions which are economically and industrially useful and practicable. Particularly preferred “reversible” reactions include those where exposing one or more byproduct compounds to hydrogen regenerates a species of a starting material hydroxide or hydride. In the same manner, a “non-reversible reaction” generally applies to both reactions that are irreversible via the reaction mechanism pathway, and also to those reactions where regenerating a species of a starting material hydride or hydroxide by exposure to hydrogen is carried out at impractical processing conditions, such as, extreme temperature, extreme pressure, or cumbersome product removal, which prevents its widespread and practical use. Endothermic hydrogen formation reactions according to the present invention are generally reversible at desirable temperature and pressure conditions.

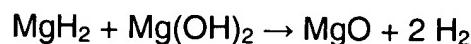
[0033] One aspect of the present invention is a reduction in the overall energy requirements for a system of storing and subsequently releasing hydrogen. Minimizing the overall enthalpy changes associated with the hydrogen storage material system results in an improvement of the overall efficiency of the fuel cell system. As the overall enthalpy change increases, so do the requirements for managing heat transfer systems (heating and cooling operations). In particular, it is highly advantageous to minimize heating and cooling systems in mobile units containing fuel cells (e.g., vehicles or electronic devices), because additional systems draw parasitic energy and increase the overall weight of the mobile unit, thereby decreasing its gravimetric efficiency.

[0034] Other advantages of minimizing overall enthalpy change in the hydrogen storage system are often realized during start-up and other transient conditions (e.g., low load conditions), because there is less diversion of energy from other important system operations. Thus, one aspect of the present invention is a minimization of the overall energy necessary to both produce and regenerate a hydrogen storage material. In preferred embodiments of the present invention, the energy required for hydrogen production and recharge is relatively low, and vastly improved when compared to energy requirements of prior art hydrogen storage systems.

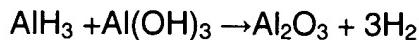
[0035] As previously discussed, one preferred embodiment of the present invention comprises a hydrogen storage composition where the hydride is lithium hydride LiH and the hydroxide is lithium hydroxide LiOH, which react with one another to form Li₂O and H₂. The enthalpy of reaction (ΔH_r) for the hydrogen production reaction was calculated based on the standard heat of formation (ΔH_f) for each of the compounds, and resulted in theoretical ΔH_r of – 23.3 kJ/mol-H₂. This ΔH_r indicates an exothermic reaction, with a relatively low enthalpy (and thus a low level of heat production). Minimizing the amount of heat released into the fuel cell system is preferred, because larger enthalpies result in larger quantities of emitted heat, which must be controlled by cooling systems to prevent damage to the surrounding environment, especially in a fuel cell system where certain components (e.g., control circuitry or the membrane exchange assembly (MEA)) potentially degrade upon exposure to higher temperatures. As the enthalpy of the reaction increases, the size and

complexity of the heat transfer system becomes much larger. Further, larger heats of reaction have the potential to be less controllable and often cannot be stopped prior to complete reaction. The present embodiment thus provides a relatively low exothermic heat of reaction for the hydrogen production reaction. An exothermic hydrogen production reaction has an advantage of not requiring a sustained input of external energy from the fuel cell system for hydrogen generation (aside from any activation energy necessary to initiate the reaction, as will be discussed in more detail below). It is preferred that the heat released by the hydrogen generation reaction is dissipated by a heat transfer system, as it is preferred to maintain the storage materials at a constant temperature during the reaction. However, the present embodiment does not require an extensive cooling system and further provides good control over the reaction as it proceeds.

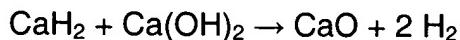
[0036] Other preferred embodiments according to the present invention have an exothermic hydrogen production reaction and include reactions between a hydride composition MI^xH_x and a hydroxide composition $MII^y(OH)_y$, where MI and MII are selected to be the same cationic species selected from the group consisting of Al, B, Be, Ca, Mg, Sr, and Ti. These reactions have a higher enthalpy of reaction ΔH_r than the previous embodiment, and include for example, the following reactions. Where the hydride is selected to be MgH_2 and the hydroxide is selected to be $Mg(OH)_2$, the reaction can be expressed as:



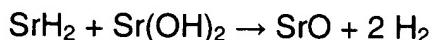
[0037] which has a ΔH_r of $-101.3 \text{ kJ/mol-H}_2$ and a theoretical hydrogen production of 4.7 wt. %. Where the hydride is selected to be AlH_3 and the hydroxide is selected to be Al(OH)_3 , the reaction can be expressed as:



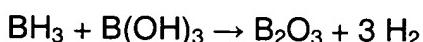
[0038] which has a ΔH_r of $-129.3 \text{ kJ/mol-H}_2$ and a theoretical hydrogen production of 5.5 wt. %. In the case where the hydride is selected to be CaH_2 and the hydroxide is selected to be Ca(OH)_2 , the reaction can be expressed as:



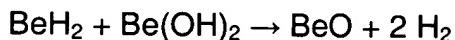
[0039] which has a ΔH_r of -53.7 kJ/mol-H_2 and a theoretical hydrogen production of 3.4 wt. %. Where the hydride is selected to be SrH_2 and the hydroxide is selected to be Sr(OH)_2 , the reaction can be expressed as:



[0040] which has a ΔH_r of -17.7 kJ/mol-H_2 and a theoretical hydrogen production of 1.9 wt. %. Where the hydride is selected to be BH_3 and the hydroxide is selected to be B(OH)_3 , the reaction can be expressed as:



[0041] which has a ΔH_r of -94.9 kJ/mol-H_2 and a theoretical hydrogen production of 7.9 wt. %. Where the hydride is selected to be BeH_2 and the hydroxide is selected to be Be(OH)_2 , the reaction can be expressed as:

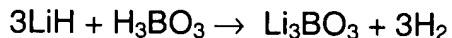


which has a ΔH_r of $-147.4 \text{ kJ/mol-H}_2$ and a theoretical hydrogen production of 7.4 wt. %.

[0042] An additional exothermic hydrogen production reaction according to the present invention comprises reacting lithium hydride (LiH) with boron hydroxide ($\text{B}(\text{OH})_3$) (which is more typically known as boric acid and expressed as H_3BO_3), which under certain pressure, temperature, and other reaction conditions proceeds by the following reaction mechanism:



which has a ΔH_r of -84.2 kJ/mol-H_2 and a theoretical hydrogen production of 6.9 wt. %. Under different pressure, temperature, and other reaction conditions, the same reactants can proceed according to the following reaction mechanism, where the oxide product differs from the two oxide products above(i.e., LiBO_2 and Li_2O), and forms a single complex higher order oxide product (Li_3BO_3):

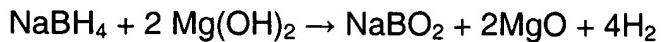


which likewise has a ΔH_r of -84.2 kJ/mol-H_2 and a theoretical hydrogen production of 6.9 wt. %.

[0043] Further preferred alternate embodiments of the present invention, are where the hydride composition is $\text{M}^{\text{x}}\text{H}_x$ and the hydroxide is $\text{M}^{\text{y}}(\text{OH})_y$, where the hydride is a complex hydride $\text{M}'_d^a(\text{M}''^b\text{H}_c)^{-d}$ where M' is selected to be lithium and M'' is selected to be boron, and the reaction is exothermic, include the following reactions. The first hydrogen production reaction occurs between:



where a theoretical 6.8 weight % of hydrogen is produced and the reaction has a ΔH_r of -22 kJ/mol-H₂. A second hydrogen production reaction with a complex hydride where M' is sodium and M" is boron, includes the reaction:



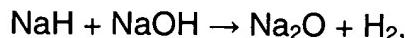
which produces a theoretical 5.2 weight % of hydrogen and a ΔH_r of -34 kJ/mol-H₂.

[0044] Another preferred embodiment of the present invention previously discussed is that where the hydride is sodium hydride (NaH) and the hydroxide is lithium hydroxide (LiOH). A calculated heat of reaction (ΔH_r) is +9.7 kJ/mol-H₂, which indicates an endothermic heat of reaction, which is relatively small. Thus, producing hydrogen with this hydrogen storage material system would require only slight heating throughout the hydrogen production reaction. However, because the overall quantity of heat generated is relatively low, this embodiment is preferred for certain applications. The endothermic nature of the hydrogen production reaction allows for an exothermic recharging reaction.

[0045] In certain applications, this hydrogen storage material composition may be preferred because the regeneration reaction is generally reversible at relatively low temperature and pressure conditions. For example, a predicted equilibrium pressure for the byproduct material comprising oxide is approximately 1 bar at 50°C, thus upon exposure to pressurized hydrogen above the equilibrium pressure, the material will absorb and react with hydrogen to regenerate a species of the hydride and hydroxide: NaH and LiOH (and

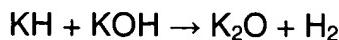
preferably both). It should be noted that in circumstances where the byproduct composition comprises a mixed cation oxide (LiNaO), the species of regenerated hydride and hydroxides may also comprise a species of hydride and hydroxide different from the starting material compositions, for example NaOH, LiH, or mixed cation hydrides and hydroxides, such as LiNa(OH)₂, for example. As recognized by one of skill in the art, when the materials are recharged to form different starting materials comprising a species of hydroxide and hydride, the hydrogen production reaction thermodynamics may change, such that the heat of reaction may likewise changes. The feasibility of recharging the hydrogen storage material with hydrogen at relatively low temperatures and pressures makes the present embodiment, and those with similar properties, desirable for mobile units, where the hydrogen storage material can be regenerated at the point-of-use (e.g., on-board), without need for further processing and reacting at an offsite facility.

[0046] Other preferred embodiments according to the present invention, where the hydrogen generation reaction is endothermic, include one where M_I and M_{II} are each selected to be sodium, such that the hydrogen production reaction proceeds according to the reaction mechanism:



that has a theoretical hydrogen production amount of 3.1 weight %. The theoretical enthalpy of reaction ΔH_r is +67.4 kJ/mol-H₂. The present embodiment is likewise useful for on-board regeneration for a mobile unit, and has a predicted equilibrium pressure of 1 bar at 475°C. Another preferred

embodiment is where M_I and M_{II} are selected to be potassium, and proceeds according to the reaction mechanism:



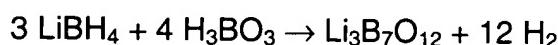
with a theoretical hydrogen generation of 2.1 weight %. The theoretical enthalpy of reaction ΔH_r for the potassium hydroxide and potassium hydride hydrogen production reaction is + 119.7 kJ/mol-H₂.

[0047] Further preferred alternate embodiments of the present invention, where the hydrogen production reaction is exothermic are where the hydride composition is M_I^xH_x and the hydroxide is M_{II}^y(OH)_y, where the hydride is selected to be a complex hydride (i.e., M'_d^a(M''_bH_c)^{-d}, for example, NaBH₄, where M' is Na and M'' is B) and the reaction is endothermic, include the following exemplary reaction:



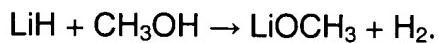
which produces a theoretical 4.0 weight % and a +21 kJ/mol-H₂.

[0048] Alternate preferred embodiments of the present invention include varying the stoichiometry of the starting material reactant hydride and hydroxide to produce higher-order complex oxide products. Thus, for example, a complex hydride, such as for example, lithium borohydride (LiBH₄) reacts with a hydroxide, for example boron hydroxide B(OH)₃ (i.e., boric acid H₃BO₃) to form a higher-order complex oxide compound according to the following reaction mechanism:



which produces the complex higher-order oxide compound $\text{Li}_3\text{B}_7\text{O}_{12}$ and a theoretical 7.6 wt. % of hydrogen.

[0049] Yet another preferred embodiment comprises a hydroxide where MII is a relatively low molecular weight organic group, such as, methyl, ethyl, and propyl groups. One example of such a hydrogen production reaction, where the hydride composition is selected to be lithium hydride (LiH) and the hydroxide composition is selected to be methanol (CH_3OH) the reaction proceeds according to the following alcoholysis mechanism:



[0050] As appreciated by one of skill in the art, any number of variations of hydride and hydroxide combinations are contemplated by the present invention, and may include any number of combinations of MI and MII selections. Further, the hydroxide compositions or the hydride compositions may comprise mixtures of hydroxide or hydride compounds. For example, the hydroxide compositions may comprise a plurality of distinct hydroxide compounds (e.g. LiOH, NaOH) mixed with one another for reacting with a hydride composition. Thus, the embodiments disclosed above are merely exemplary of a wide range of species which are useful with the hydrogen storage material composition of the overall present invention.

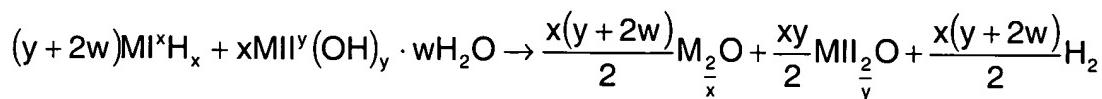
[0051] Another preferred embodiment of the present invention provides a hydroxide composition which comprises a hydrated hydroxide which reacts with a hydride. Many hydroxide compounds readily form hydrated compounds, due to their hydroscopic nature. It is preferred that the hydrated hydroxide

compound comprises at least a portion of the hydroxide compound (i.e., that the starting material hydroxide is a mixture of non-hydrated hydroxide and hydrated hydroxide), or in an alternate embodiment that hydrated hydroxide comprises all of the hydroxide composition starting material. A hydrated hydroxide increases the density of hydrogen stored within the hydrogen storage material increases hydrogen content, but likewise increases the weight of the material and potentially increases the heat evolved. The heat evolved from the hydrated hydroxide compounds may be beneficial to offset certain endothermic reaction systems, thereby reducing the overall enthalpy and heat of reaction.

[0052] Although not wishing to be bound by any particular theory, it is theorized that the water of hydration attached to the hydroxide reacts with a portion of the hydride in a first exothermic initiation reaction, which produces heat and hydroxide. The remaining portion of hydride (now dehydrated) is available to react in a hydrogen production reaction with the hydroxide. Thus, the starting material compositions comprise a hydride $M^{I\!I}H_x$ and a hydrated hydroxide $M^{I\!I}^{y+}(OH)_y \cdot wH_2O$, where y represents the average valence state of $M^{I\!I}$ to maintain charge neutrality of the hydroxide compound and w represents a stoichiometric amount of water. A first portion of the hydride reacts with the hydration water to provide heat to the surrounding starting material and to form a hydroxide product. The remaining portion of the hydride reacts with the hydroxide which comprises the newly formed product from the initiation reaction, as well as the initial hydroxide provided in the starting material. Thus, the heat

of reaction is more exothermic in the embodiment where the hydroxide is hydrated, versus the embodiment where the hydroxide is dehydrated.

[0053] The reaction proceeds according to the following:



where as previously discussed, x is the average valence state of M\text{I} and y is the average valence state of M\text{II}, where the average valence state maintains the charge neutrality of the compound, and where w is a stoichiometric amount of water present in the hydrated hydroxide compound.

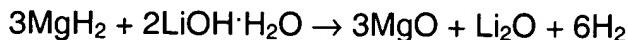
[0054] Preferred hydride compositions for the present embodiment are the same as those described above in previous embodiments. Particularly preferred hydride compounds comprise LiH, LiBH₄, NaBH₄, MgH₂, NaH, and mixtures thereof. Preferred hydrated hydroxide compounds comprise primarily the same cationic species as those discussed in the non-hydrated hydroxide embodiments above, including aluminum (Al), arsenic (As), boron (B), barium (Ba), beryllium (Be), calcium (Ca), cadmium (Cd), cerium (Ce), cesium (Cs), copper (Cu), europium (Eu), iron (Fe), gallium (Ga), gadolinium (Gd), germanium (Ge), hafnium (Hf), mercury (Hg), indium (In), potassium (K), lanthanum (La), lithium (Li), magnesium (Mg), manganese (Mn), sodium (Na), neodymium (Nd), nickel (Ni), lead (Pb), praseodymium (Pr), rubidium (Rb), antimony (Sb), scandium (Sc), selenium (Se), silicon (Si), samarium (Sm), tin (Sn), strontium (Sr), thorium (Th), titanium (Ti), thallium (Tl), tungsten (W), yttrium (Y), ytterbium (Yb), zinc (Zn), zirconium (Zr), and mixtures thereof.

[0055] Preferred hydrated hydroxide compounds according to the present invention include, by way of example, Ba(OH)₂·3H₂O, Ba(OH)₂·H₂O, KOH·H₂O, NaOH·H₂O. Particularly preferred hydrated hydroxide compounds comprise: LiOH·H₂O and NaOH·H₂O. The hydrated hydroxide may also form a complex cationic hydrated hydroxide compound comprising complex cationic species, such that MII comprises two cationic species. Examples of such complex cationic hydrated hydroxide compounds include, LiAl₂(OH)₇·2H₂O and Mg₆Al₂(OH)₁₈·4H₂O. It should be noted that the quantity of water in the hydrated compound may comprise more than one molecule of water (i.e., that w, the stoichiometric ratio of water, may vary), depending on the hydroxide compound and its propensity for hydration. The present invention further contemplates mixtures of hydrated hydroxide compounds (as well, as alternate embodiments having mixtures of hydrated and non-hydrated hydroxide compounds, which were previously described above).

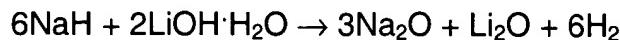
[0056] Certain preferred reactions according to the present embodiment, include those where a hydrated hydroxide compound reacts with a hydride compound. The following non-limiting examples are where the hydride composition is MI^xH_x and the hydrated hydroxide is represented by MII_y(OH)_y·zH₂O, and where MII is selected to be lithium:



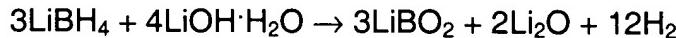
which produces a theoretical 9.0 weight % and a ΔH_r of -45.2 kJ/mol-H₂. Another reaction according to the present embodiment is where:



which produces a theoretical 7.4 weight % and a ΔH_r of -99 kJ/mol-H₂. Yet another reaction with a hydrated hydroxide is as follows:

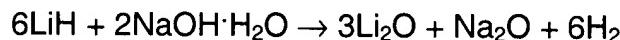


which produces a theoretical 5.3 weight % and a ΔH_r of +11 kJ/mol-H₂. Yet another reaction is:



which produces a theoretical 10.2 weight % and an exothermic ΔH_r of -43.5 kJ/mol-H₂.

[0057] Similar examples of reactions where the hydrated hydroxide comprises MII selected to be sodium proceed as follows:

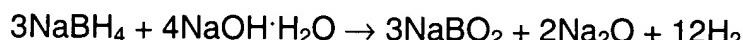


which produces a theoretical 7.3 weight % and an exothermic ΔH_r of -34.2 kJ/mol-H₂. A similar reaction which is endothermic is as follows:



which produces a theoretical 4.6 weight % and a ΔH_r of +22.0 kJ/mol-H₂.

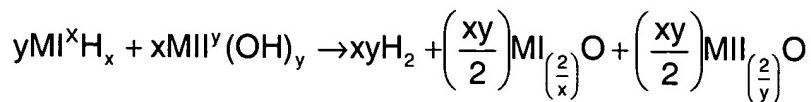
Another preferred exothermic reaction is as follows:



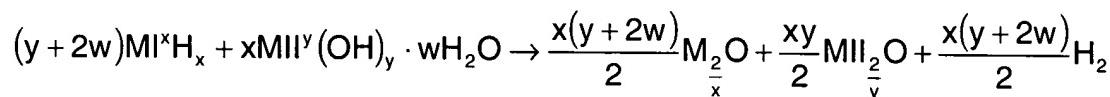
which produces a theoretical 6.9 weight % and an exothermic ΔH_r of -21.4 kJ/mol-H₂.

[0058] Alternate preferred embodiments of the present invention contemplate a mixture of starting material hydroxide comprising hydrated hydroxide and non-hydrated hydroxide starting materials which react with hydrides to produce hydrogen and a “complex oxide”, meaning the oxide has

higher order atomic ratio of oxygen to cationic species as compared to the simple oxides of the previous embodiments, as recognized by one of skill in the art. Such a reaction system includes both the general reaction of the hydride plus hydroxide (a first hydrogen generation reaction)



and the hydride plus hydrated hydroxide (a second hydrogen generation reaction)

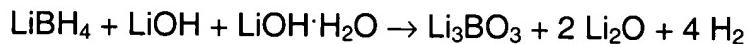


where the starting reactant material compositions, comprising hydrides, hydroxides, and hydrated hydroxides, can be combined in any number of proportions to conduct both the first and second hydrogen generations concurrently. With such a combination of reactions, the amount of heat release can be designed by accounting for the quantities of reactants added and the corresponding heat of reaction for both the first and second hydrogen production reactions. Generally, the second hydrogen generation reaction where hydrated hydroxide reacts with a hydride is generally more exothermic than the first hydrogen generation reaction where a non-hydrated hydroxide reaction with a hydride.

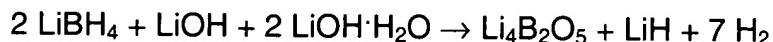
[0059] Thus, reaction systems, such as those described above, comprise a combination of reactions for both hydrated hydroxide and non-hydrated hydroxides that are useful in designing a reaction to have a targeted

overall heat of reaction. As previously discussed, one aspect of the present invention is the minimization of the overall enthalpy of the reaction system, which can be further controlled by adding a selected mass of hydrated hydroxide to the starting material mixture. Further, the hydrated hydroxides contain a greater amount of hydrogen per formula unit, and mixtures of hydrated hydroxides with non-hydrated hydroxides can be designed for larger hydrogen production due to a larger quantity of hydrogen present in the starting materials.

[0060] Examples of such combined reaction systems, where both the hydrides of the first and second hydrogen production reactions are selected to be the same, and a hydroxide composition comprises both hydrated and non-hydrated hydroxides both having the same cationic species such as where the cationic species of the hydride is lithium (LiH) and the hydroxides also have lithium (LiOH) according to the present invention, can be expressed in the simplified reaction mechanism:



which generates an oxide (Li₂O) and a complex oxide (Li₃BO₃) and a theoretical 9.0 % by weight of hydrogen. Yet another example, where the reactants are the same, but provided at a different stoichiometry, produces different products in the following reaction:



which generates a complex oxide (Li₄B₂O₅), a simple hydride (LiH) and a theoretical 9.2% by weight hydrogen.

[0061] The present invention provides a mixture of a hydride and a hydroxide having cationic species other than hydrogen, each one characterized by promoting the release of hydrogen from the other one, in the presence of: a catalyst, elevated temperature, or both.

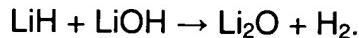
[0062] The present invention also provides a method of producing a source of hydrogen gas comprising liberating hydrogen from a hydrogenated starting material comprising a hydride and a hydroxide, where the hydroxide has one or more cationic species other than hydrogen and by reacting the hydride with the hydroxide to produce a dehydrogenated product and hydrogen gas. In certain preferred embodiments, the hydrogenated starting material composition can be regenerated by exposing the dehydrogenated product (which preferably comprises an oxide composition) to hydrogen gas. As the liberating proceeds, it is preferred that the hydrogen gas is removed, both to collect the hydrogen gas as fuel for the fuel cell, and in some reaction systems to drive the reaction forward. The liberation of hydrogen gas can be conducted in the presence of an appropriate catalyst contacting the starting material composition to facilitate hydrogen release.

[0063] In preferred embodiments of the present invention, a hydrogen production reaction is conducted by a solid-state reaction, where the starting materials are in particulate form. The desirable particle size of the starting materials is related to its hydrogen release performance. Particles which are too coarse extend the time for the hydrogen release reaction at a given temperature. As will be discussed in more detail below, a smaller particle size

may contribute to overcoming activation energy barriers by increasing the surface area interface between the hydrogenated starting material reactants. Further, it is preferred that the starting material reactants are essentially homogeneously mixed together, to enhance the reactivity of the mixture of hydrogenated starting material reactants. By "essentially homogeneously mixed" it is meant that the different starting material reactants are distributed with one another sufficiently that the reaction rate is not significantly inhibited by isolation of reactant particles from one another. It is preferred that starting material particles have a size on the order of 100 micrometers (μm), which can be achieved by ball milling for 1 to 10 hours, for example, to form a suitable starting material. Preferably the particle size of the reactants is on the order of less than about 10 micrometers, and most preferably less than 1 micrometer.

[0064] EXAMPLE 1

[0065] This example demonstrates the hydrogen storage material system where M_I and M_{II} are selected to be lithium in the hydrogen storage material system. An equal molar ratio of lithium hydride (LiH) and lithium hydroxide (LiOH) were weighed at 0.248 g of LiH and 0.756 g of LiOH and were mixed to form the hydrogenated mixture the hydrogen storage media system, that releases hydrogen according to the following reaction to produce hydrogen:



The mixing was accomplished using standard ball milling techniques at room temperature under ambient conditions for 60 minutes. Some hydrogen generation was noted during the milling process. The mixture was then heated

at a rate of 2°C per minute up to a maximum temperature of 300°C while under ambient conditions and analyzed by a modified Sievert's apparatus, where the volumetric gas absorption is measured and converted to a weight percentage.

[0066] This analysis is shown in Figure 1, where a total of 5.3 weight % was generated (with the difference between the theoretical 6.25 weight % being attributed to the hydrogen generated and either lost during the milling process or due to impurities in the starting materials). From the graph, it is apparent that hydrogen generation begins at about 80°C and accelerates at approximately 170°C.

[0067] EXAMPLE 2

[0068] The hydrogen storage material system is the same as that in Example 1. Equal molar ratios of lithium hydroxide (LiOH) and lithium hydride (LiH) with measured amounts of 0.249 g LiH and 0.749 g of LiOH were mixed together and mechanically milled using the same ball milling techniques as described in Example 1, except that the mixture was milled for a shorter duration of 12 minutes.

[0069] EXAMPLE 3

[0070] A hydrogen storage material system where the hydride is lithium hydride (LiH) and the hydroxide is lithium hydroxide (LiOH), similar to Example 2 above, is reacted in the presence of a catalyst, titanium chloride, TiCl₃. A mixture of an equal molar ratio of lithium hydride (LiH) and lithium hydroxide (LiOH) weighed as 0.201g LiH and 0.611g of LiOH were mixed with one

another. The catalyst was further added during milling at 10 mol % weighed at 0.385 TiCl₃, and the entire mixture was then milled for 12 minutes.

[0071] The resulting samples from Examples 2 and 3 were subjected to a modified Sievert's analysis, where heat was applied in increasing steps. The first heating step reached a temperature of 100°C (point A), the second step ramps up to 200°C (point B) and then the final step reached 250°C (point C). As can be observed from the data, the hydrogen generation began at approximately 80°C for the Sample from Example 2 without a catalyst. As the temperature was held constant through the first step at 100°C, the rate of hydrogen generation in the Example 2 Sample slowed reaching only approximately 0.7 weight percent. Increasing the temperature to the next step of 200°C increased the amount of hydrogen generated, but as the sample remained at 200°C the rate of hydrogen generation slowed. As the sample temperature was again elevated, to the 250°C interval, a similar behavior was observed, where hydrogen production slowed at constant temperature. After increasing to 250°C, 5.7 wt. % of hydrogen was generated. This amount is closer to the theoretical hydrogen amount of 6.25 wt. % and the amount in Example 1, and is attributed to less hydrogen generated or lost during the milling process.

[0072] The data shown in Figure 2 suggests that there is an activation energy barrier for this exothermic reaction that occurs at about 80°C, where the hydrogen release initiates. As can be observed from the data, the presence of a catalyst during the hydrogen generation reaction significantly accelerates

hydrogen evolution. For example, at 100°C, only approximately 0.7 wt. % hydrogen was produced for the mixture made in Example 2 without a catalyst, as where approximately 2.7 wt. % hydrogen was generated at 100°C for the mixture of Example 3 with 10 mol. % catalyst. The overall lower quantity of hydrogen produced in the Example 3 sample is likely attributed to premature production of hydrogen during the milling process.

[0073] The behavior of the hydrogen storage material system in both Figures 1 and 2 shows that the hydrogen production reaction is kinetically limited. The sample from Example 3 where the catalyst was added demonstrates that the catalyst facilitates greater hydrogen release at relatively low temperatures. Due to the fact that the hydrogen production reaction in the lithium hydride and lithium hydroxide system is exothermic, the thermodynamic equilibrium state corresponds to a nearly complete reaction at room temperature. It is also possible that product (such as, solid phase byproduct oxide composition or hydrogen gas) accumulating where the reaction is occurring in the hydrogen storage material mixture may inhibit full release of hydrogen from the storage material. The reaction can be driven towards complete release of hydrogen by addressing both the activation energy barrier and the inhibition by product build-up through various means recognized by one of skill in the art.

[0074] For example, as previously discussed, mixing the solid reactant particles in an essentially homogenous mixture on a fine scale facilitates greater hydrogen release from the hydrogen storage compositions. Also, suitable

catalysts (such as the TiCl₃ in Example 3) may be selected to facilitate the reaction and drive it to completion by overcoming any initiation/activation energy barriers. Exemplary catalysts suitable for use with the present invention include for example, compounds comprising elements selected from the group consisting of Ti, V, Cr, C, Fe, Mn, Ni, Si, Al, Nb, Pd, and mixtures thereof. Such catalyst compounds may be selected in elemental form, or may comprise hydride, halide, oxide, or nitride compounds, for example. A non-limiting list of such catalyst compounds includes: TiCl₃, TiO₂, TiN, V₂O₅, SiO₂, Nb₂O₅, and Al₂O₃, for example.

[0075] Further, products may be removed as the reaction proceeds. For example, hydrogen gas will easily be removed, and methods of solid-solid separation recognized by one of skill in the art may be employed to address the accumulation of solid phase oxide compositions in the hydrogen storage materials. Additionally, as will be discussed in greater detail below, one preferred embodiment of the present invention initiates the hydrogen production reaction by providing heat via a second exothermic reaction to overcome the activation energy barrier of the hydrogen production reaction. This exothermic initiation reaction transfers heat to the solid-state reactants in an amount sufficient to initiate the subsequent hydrogen generation reaction with one another.

[0076] EXAMPLE 4

[0077] In Example 4, a mixed cation hydrogen storage material system is provided where M_I is selected to be sodium and M_{II} is selected to be lithium.

An equal molar ratio of sodium hydride (NaH) and lithium hydroxide (LiOH) weighed as 0.655g NaH and 0.652g of LiOH, was mixed and ground by conventional ball milling techniques. A considerable amount of hydrogen generation was noted during the milling process (by an audible gas release when opening the milling vessel). The milled mixture was then analyzed by a modified Sievert's apparatus as shown in Figure 3. As can be observed from the data, hydrogen generation begins at approximately 40°C (point A) and is complete at approximately 100°C (point B). Approximately 0.8 wt. % of hydrogen was generated, which is less than the theoretical yield of 4.1 weight percent, however as noted above, a large unquantified amount of hydrogen was produced during milling, which would likely approach the theoretical yield when accounted for.

[0078] EXAMPLE 5

A mixed cation hydrogen storage material system where the hydride is a complex hydride (i.e., lithium borohydride where M_I is selected to be lithium) and a hydroxide where M_{II} is selected to be lithium forming lithium hydroxide. An equal molar ratio of lithium borohydride (LiBH₄) and lithium hydroxide (LiOH) weighed as 0.224g LiBH₄ and 0.981g of LiOH, was mixed and then milled for 1 hour. The sample of Example 5 was analyzed by a modified Sievert's analysis as the results shown in Figure 4. Hydrogen generation appears to commence at approximately 250°C, however, with addition of a catalyst (such as in Example 3), the reaction kinetics should be modified to produce hydrogen at lower

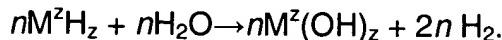
temperatures. A maximum of 6.6 wt. % hydrogen was produced, which is close to the theoretical yield of 6.8 wt. %.

[0079] In accordance with the behavior observed during the Sievert's testing of the hydrogen storage material systems, it is preferred that the hydrogen production reaction between the hydroxide compositions and hydride compositions is conducted at an elevated temperature above ambient conditions, primarily to increase the rate of reaction, as well as overcoming any initiation activation barriers. Although this specific temperature varies for the thermodynamics of the particular reaction, which is dependent upon the cationic species selected, certain preferred embodiments of the present invention conduct a reaction at a temperature of above about 40° C. Other preferred embodiments of the present invention preferably are conducted at a temperature of about 80° C or higher.

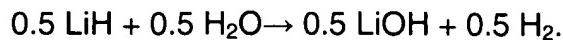
[0080] Additionally, a compressive force may be applied on the solid starting materials while conducting the hydrogen production reaction of the present invention to increase physical contact between the particles and to enhance the reaction. However, in such an embodiment where compressive force is applied to the starting materials, it is preferred that the compressive force is applied in such a manner so as not to prevent hydrogen gas formation or release. For example, the compressive force may be applied with platens formed of porous material, which permits gas to travel therethrough, as it is generated within the starting materials.

[0081] The present invention further provides a method of producing hydrogen which comprises reacting a first portion of a starting material comprising a hydride with water. This first initiation reaction between the first portion of the hydride and water is spontaneous and exothermic, generating approximately 165 kJ/mol-H₂ in the heat of reaction, which provides heat to the surrounding starting materials. This generated heat provides the necessary enthalpy to overcome the energy activation barrier of the hydrogen production reaction between a remaining second portion of hydride and a hydroxide. The hydrogen production reaction may be exothermic or endothermic. The first reaction commences the second reaction, and in certain preferred embodiments, the first reaction proceeds essentially simultaneously or concurrently with the second reaction.

[0082] The total amount of hydride present in the starting material comprises the first and second portions. In preferred embodiments of the present invention, the total amount of hydride present in the starting material, includes the first portion which reacts with water in a molar amount designated "n", so that in the example where MI and MII are the same cationic species, M, having an average valence state of "w" the initiation reaction would proceed by the following mechanism:

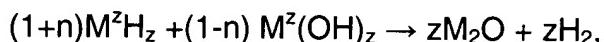


For example, where the cationic species MI and MII are selected to be lithium (Li) for both the hydride and hydroxide, and n = 0.5, the reaction can be expressed as

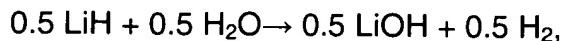


The molar amount of hydride added is preferably correlated to how much heat is needed to initiate the second hydrogen production reaction, and depends upon the overall mass of reactants present in the starting material for the second hydrogen production reaction. The value of "n" can be adjusted to heat the starting material mixture to the desired reaction initiation temperature.

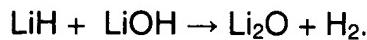
[0083] The first initiation reaction generates "n" moles of hydroxide, produced by a reaction between "n" moles of water and "n" moles of hydride. To account for the hydride consumed in the first reaction with water, as well as the hydroxide produced by the first reaction, the starting hydrogen storage materials in the hydrogen production reaction can be adjusted by the following molar proportions:



where n moles of hydride is consumed in the heat generation reaction, while reacting with n moles of water to generate and n moles of hydroxide, where z moles of oxide and hydrogen are each produced, such that the molar amount of hydride consumed in the initiation reaction (and corresponding to a sufficient enthalpy to initiate the second reaction) or the hydroxide formed in the heat generation reaction is compensated for in the second reaction. Thus, in the heat generation reaction, where $n = 0.5$, the reaction proceeds as



where 0.5 LiH was consumed as a first portion of the hydride starting material and 0.5 LiOH was generated for use in the hydrogen production reaction. Thus, the hydrogen production reaction proceeds according to:



[0084] It is preferred that the hydrogen production reaction proceeds to substantial completion and that the hydride (and likewise the hydroxide) reactant is substantially consumed. By “substantial” and “substantially”, it is meant that the reaction proceeds and reactant are consumed in the reaction to an industrially practical level, expected by one of skill in the art. Thus, the resulting mixture has the exact stoichiometry needed for the hydrogen production reaction to proceed essentially to completion by essentially all of the reactants forming products. Further, the molar amount of hydroxide generated in the first initiation reaction is likewise accounted for in the second hydrogen production reaction. It should be noted that the present invention is equally applicable to situations where M_I and M_{II} are selected to be different cationic species from one another, and as one of skill in the art would appreciate, the hydroxide generated may form a mixture of hydroxide reactants (e.g., $n\text{M}_I^x(\text{OH})_x$ and $\text{M}_{II}^y(\text{OH})_y$ which combined together, respectively react with the hydride M_I^xH_x), which likewise generate a byproduct compound in the second hydrogen generation reaction that comprises mixtures of oxide compositions (having mixed cationic species, or mixtures of distinct oxide compositions with different

cationic species). Such alternate preferred embodiments where MI and MII are different from one another, may result in a modification to the thermodynamics of the hydrogen production reaction, by introducing another reactant into the reaction, as appreciated by one of skill in the art. Thus, in the present embodiment of the present invention, a total amount of hydride in the starting material composition comprises the first and second portions of the hydride, where the first portion reacting with water is preferably dictated by the amount of thermal energy necessary to initiate and cause the hydrogen production reaction, and the second portion of hydride is an amount sufficient to react with both the hydroxide generated in the initiation reaction and the amount provided for the hydrogen production reaction.

[0085] Alternate preferred embodiments may include additional amounts of a particular reactant, not in accordance with the molar stoichiometry discussed in the embodiment above, such as for example, providing excess hydride for ensuring the reaction proceeds to completion. Other considerations may include providing more reactant in reactions where the presence of the reactant impact the reaction rate, or the reactant may have physical limitations, such as a larger particle size or difficulty in homogeneously mixing.

[0086] Preferred embodiments of the present invention thus provide a method of producing hydrogen by generating heat in a first reaction by reacting water with a portion of a hydride present in a first material composition, wherein the heat is used in a second hydrogen production reaction. A remaining portion of the hydride present in the first material composition is reacted with a

hydroxide having one or more cations other than hydrogen present in a second material composition by a hydrogen production reaction, which forms a hydrogen product and a byproduct composition comprising an oxide. One preferred aspect of the present invention is that the combined hydrogen storage system, including a water initiation reaction, is hydrogen rich. The water reacting with hydride also produces hydrogen, which increases the total amount of hydrogen produced by the hydrogen storage material system.

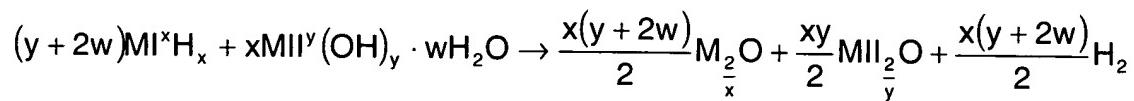
[0087] The water for the first exothermic initiation reaction may be added to the solid phase starting material mixture, as a liquid reactant. It is preferred that the water is generally evenly distributed throughout the starting material mixture to provide even heat to the surrounding particles. However, in alternate embodiments where the hydrogen production reaction is exothermic, it is possible that only a relatively small portion of the starting material hydride is heated to above the reaction initiation temperature. As the initiation temperature causes the hydrogen production reaction in nearby reactant particles, heat will be generated by the hydrogen production reaction, and further be transferred to the surrounding starting material, thus providing the necessary activation energy to start the hydrogen production reaction in the surrounding material.

[0088] In alternate preferred embodiments of the present invention, the water may be provided as water of hydration in one of the starting materials. The water of hydration then reacts with the hydride material. It is preferred that the hydrated compound is the hydroxide compound, many of which are hydroscopic and readily form hydrated compounds. Although not wishing to be

limited by any particular theory, it appears that the water of hydration attached to the hydroxide reacts with a portion of the hydride in a first exothermic initiation reaction, which produces heat and hydroxide. The remaining portion of hydride (now dehydrated) is available to react in a hydrogen production reaction with the hydroxide. The water of hydration attached to the hydroxide reacts with a portion of the hydride in a first exothermic initiation reaction, which produces heat and hydroxide.

[0089] Thus, the starting material mixture has a hydrated hydroxide and a hydride mixed together with one another. The starting material compositions comprise a hydride MI^xH_x and a hydrated hydroxide $MII_y(OH)_y \cdot wH_2O$, where y represents the average valence state of MII to maintain charge neutrality of the hydroxide compound and w represents a stoichiometric amount of water. A first portion of the hydride reacts with the hydration water to provide heat to the surrounding starting material and to form a hydroxide product. The remaining portion of the hydride reacts with the hydroxide which comprises the newly formed product from the initiation reaction, as well as the initial hydroxide provided in the starting material. In the present embodiment, it is contemplated that the heat generation reaction and the hydrogen production reaction behave as one reaction, rather than two distinct reactions.

[0090] The reaction proceeds according to the following:



where as previously discussed, x is the average valence state of M_I and y is the average valence state of M_{II}, where the average valence state maintains the charge neutrality of the compound, and where w is a stoichiometric amount of water present in the hydrated hydroxide compound.

[0091] Preferred hydride compositions for the present embodiment are the same as those described above in previous embodiments. Particularly preferred hydride compounds comprise LiH, LiBH₄, NaBH₄, MgH₂, NaH, and mixtures thereof. Preferred hydrated hydroxide compounds comprise primarily the same cationic species as those discussed in the non-hydrated hydroxide embodiments above, including aluminum (Al), arsenic (As), boron (B), barium (Ba), beryllium (Be), calcium (Ca), cadmium (Cd), cerium (Ce), cesium (Cs), copper (Cu), europium (Eu), iron (Fe), gallium (Ga), gadolinium (Gd), germanium (Ge), hafnium (Hf), mercury (Hg), indium (In), potassium (K), lanthanum (La), lithium (Li), magnesium (Mg), manganese (Mn), sodium (Na), neodymium (Nd), nickel (Ni), lead (Pb), praseodymium (Pr), rubidium (Rb), antimony (Sb), scandium (Sc), selenium (Se), silicon (Si), samarium (Sm), tin (Sn), strontium (Sr), thorium (Th), titanium (Ti), thallium (Tl), tungsten (W), yttrium (Y), ytterbium (Yb), zinc (Zn), zirconium (Zr), and mixtures thereof.

[0092] Preferred hydrated hydroxide compounds according to the present invention include, by way of example, Ba(OH)₂·3H₂O, Ba(OH)₂·H₂O, KOH·H₂O, NaOH·H₂O. Particularly preferred hydrated hydroxide compounds comprise: LiOH·H₂O and NaOH·H₂O. The hydrated hydroxide may also form a complex cationic hydrated hydroxide compound comprising complex cationic

species, such that MII comprises two cationic species. Examples of such complex cationic hydrated hydroxide compounds include, $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$ and $\text{Mg}_6\text{Al}_2(\text{OH})_{18} \cdot 4\text{H}_2\text{O}$. It should be noted that the quantity of water in the hydrated compound may comprise more than one molecule of water (i.e., that z , the stoichiometric ratio of water, may vary), depending on the hydroxide compound and its propensity for hydration. The present invention further contemplates mixtures of hydrated hydroxide compounds (as well, as alternate embodiments having mixtures of hydrated and non-hydrated hydroxide compounds, which were previously described above).

[0093] Further, for many hydride and hydrated hydroxide species there is a greater energy activation barrier than for the independent reactant water to the heat generation reaction, which requires additional heat or other means to overcome the initiation barrier to commence the heat generation reaction. This additional energy may include the energy required to disassociate the hydrated water molecules from the hydroxide molecules. Such initiation energy may be provided by any known means, as previously discussed (e.g., heat, reduced particle size, catalysts, and the like) or by adding some liquid water to generate heat to start the reactions between the hydrated hydroxide and the hydride. Thus, a first portion of water may be in the form of a hydrated hydroxide and a second portion of water may be provided as a liquid reactant added to the hydrated hydroxide and hydride materials.

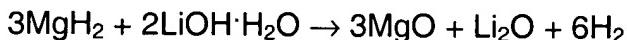
[0094] In preferred embodiments of the present invention, It is preferred that the hydrated hydroxide compound comprises at least a portion of

the hydroxide compound (i.e., that the starting material hydroxide is a mixture of non-hydrated hydroxide and hydrated hydroxide), or in an alternate embodiment that hydrated hydroxide comprises all of the hydroxide composition starting material. A hydrated hydroxide increases the density of hydrogen stored within the hydrogen storage material increases hydrogen content, but likewise increases the weight of the material and potentially increases the heat evolved. Generally, the heat of reaction is more exothermic in the embodiment where the hydroxide is hydrated, versus the embodiment where the hydroxide is dehydrated. The heat evolved from the hydrated hydroxide compounds may be beneficial to offset certain endothermic reaction systems, thereby reducing the overall enthalpy and heat of reaction.

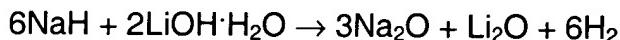
[0095] Certain preferred reactions according to the present embodiment, include those where a hydrated hydroxide compound reacts with a hydride compound. The following non-limiting examples are where the hydride composition is $M^{I\!X}H_x$ and the hydrated hydroxide is represented by $M^{II\!Y}(OH)_y \cdot wH_2O$, and where MII is selected to be lithium:



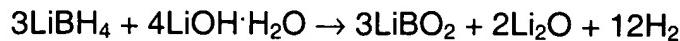
which produces a theoretical 9.0 weight % and a ΔH_r of -45.2 kJ/mol-H₂. Another reaction according to the present embodiment is where:



which produces a theoretical 7.4 weight % and a ΔH_r of -99 kJ/mol-H₂. Yet another reaction with a hydrated hydroxide is as follows:

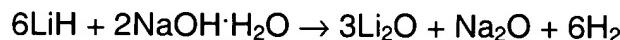


which produces a theoretical 5.3 weight % and a ΔH_r of +11 kJ/mol-H₂. Yet another reaction is:

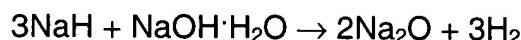


which produces a theoretical 10.2 weight % and an exothermic ΔH_r of -43.5 kJ/mol-H₂.

[0096] Similar examples of reactions where the hydrated hydroxide comprises MII selected to be sodium proceed as follows:

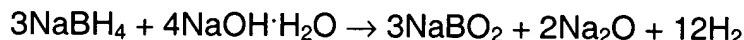


which produces a theoretical 7.3 weight % and an exothermic ΔH_r of -34.2 kJ/mol-H₂. A similar reaction which is endothermic is as follows:



which produces a theoretical 4.6 weight % and a ΔH_r of +22.0 kJ/mol-H₂.

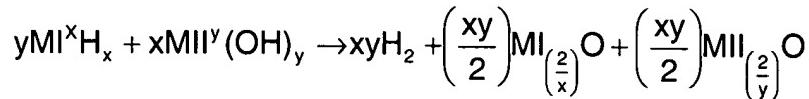
Another preferred exothermic reaction is as follows:



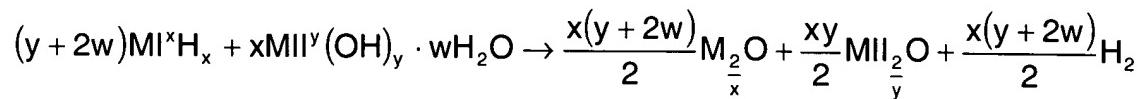
which produces a theoretical 6.9 weight % and an exothermic ΔH_r of -21.4 kJ/mol-H₂.

[0097] Alternate preferred embodiments of the present invention contemplate a mixture of starting material hydroxide comprising hydrated hydroxide and non-hydrated hydroxide starting materials which react with hydrides to produce hydrogen and a “complex oxide”, meaning the oxide has higher order atomic ratio of oxygen to cationic species as compared to the simple oxides of the previous embodiments, as recognized by one of skill in the

art. Such a reaction system includes both the general reaction of the hydride plus hydroxide (a first hydrogen generation reaction)



and the hydride plus hydrated hydroxide (a second hydrogen generation reaction)

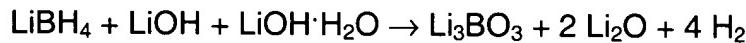


where the starting reactant material compositions, comprising hydrides, hydroxides, and hydrated hydroxides, can be combined in any number of proportions to conduct both the first and second hydrogen generations concurrently. With such a combination of reactions, the amount of heat release can be designed by accounting for the quantities of reactants added and the corresponding heat of reaction for both the first and second hydrogen production reactions. Generally, the second hydrogen generation reaction where hydrated hydroxide reacts with a hydride is generally more exothermic than the first hydrogen generation reaction where a non-hydrated hydroxide reaction with a hydride.

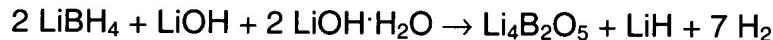
[0098] Thus, reaction systems, such as those described above, comprise a combination of reactions for both hydrated hydroxide and non-hydrated hydroxides that are useful in designing a reaction to have a targeted overall heat of reaction. As previously discussed, one aspect of the present invention is the minimization of the overall enthalpy of the reaction system,

which can be further controlled by adding a selected mass of hydrated hydroxide to the starting material mixture. Further, the hydrated hydroxides contain a greater amount of hydrogen per formula unit, and mixtures of hydrated hydroxides with non-hydrated hydroxides can be designed for larger hydrogen production due to a larger quantity of hydrogen present in the starting materials.

[0099] Examples of such combined reaction systems, where both the hydrides of the first and second hydrogen production reactions are selected to be the same, and a hydroxide composition comprises both hydrated and non-hydrated hydroxides both having the same cationic species such as where the cationic species of the hydride is lithium (LiH) and the hydroxides also have lithium (LiOH) according to the present invention, can be expressed in the simplified reaction mechanism:



which generates an oxide (Li₂O) and a complex oxide (Li₃BO₃) and a theoretical 9.0 % by weight of hydrogen. Yet another example, where the reactants are the same, but provided at a different stoichiometry, produces different products in the following reaction:



[00100] which generates a complex oxide (Li₄B₂O₅), a simple hydride (LiH) and a theoretical 9.2% by weight hydrogen.

[00101] Thus, the hydrogen storage materials according to the present invention provide solid phase hydrogen storage, which is especially advantageous in fuel cell applications, particularly in mobile fuel-cell

applications. Such hydrogen storage material compositions are generally widely available, and of relatively low molecular weight, which facilitates improving the efficiency of the fuel-cell unit. Additionally, the system of hydrogen production reactions available from the variants of the present invention have relatively low total enthalpy changes, which reduces the need for extensive control and cooling systems, as well as eliminating parasitic energy demands from the fuel-cell system. Further, the release of hydrogen from the hydrogen storage material systems is readily facilitated by an exothermic initiation reaction with a commonly available hydrogen containing reactant (i.e., water).

[00102] The description of the invention is merely exemplary in nature and, thus, variations that do not depart from the gist of the invention are intended to be within the scope of the invention. Such variations are not to be regarded as a departure from the spirit and scope of the invention.